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Stratospheric observations of CH_3D and HDO from ATMOS infrared solar spectra: Enrichments of deuterium in methane and implications for HD

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Abstract. Stratospheric mixing ratios of CH_3D from 100 mb to 17mb (≈15 to 28 km) and HDO from 100 mb to 10 mb (≈15 to 32 km) have been inferred from high resolution solar occultation infrared spectra from the Atmospheric Trace MOlecule Spectroscopy (ATMOS) Fourier-transform interferometer. The spectra, taken on board the Space Shuttle during the Spacelab 3 and ATLAS-1, -2, and -3 missions, extend in latitude from 70°S to 65°N. We find CH_3D entering the stratosphere at an average mixing ratio of $(9.9\pm0.8)\times10^{-10}$ with a D/H ratio in methane (7.1±7.4)% less than that in Standard Mean Ocean Water (SMOW) (1σ combined precision and systematic error). In the mid to lower stratosphere, the average lifetime of CH_3D is found to be (1.19±0.02) times that of CH_4, resulting in an increasing D/H ratio in methane as air "ages" and the methane mixing ratio decreases. We find an average of (1.0±0.1) molecules of stratospheric HDO are produced for each CH_3D destroyed (1σ combined precision and systematic error), indicating that the rate of HDO production is approximately equal to the rate of CH_3D destruction. Assuming negligible amounts of deuterium in species other than HDO, CH_3D and HD, this limits the possible change in the stratospheric HD mixing ratio below about 10 mb to be ±0.1 molecules HD created per molecule CH_3D destroyed.

Introduction

In the stratosphere, H_2O is created primarily by oxidation of CH_4 and H_2 by OH, Cl and $O(^1D)$. Likewise, oxidation of CH_3D and HD creates HDO, but these deuterated species show a sufficiently different reactivity with surrounding chemical species so that their measurement can provide additional insight into the stratospheric hydrogen budget. In understanding the deuterium budget of the stratosphere and relating it to the hydrogen budget, several questions arise. First, what is the lifetime of CH_3D compared to that of CH_4, or put another way, how does the D/H ratio in methane vary with the CH_4 mixing ratio? Second, is the rate of stratospheric HDO production balanced by that of CH_3D oxidation? If not, could there be a net production or destruction of HD, and possibly a change in the D/H ratio of molecular hydrogen, due to a difference in the rates between CH_3D oxidation to HD and HD oxidation to HDO? (Discussion of the D/H ratio in stratospheric water is in an accompanying paper by *Moyer et al.* [this issue].)

We address these questions using spectroscopic measurements of stratospheric CH_3D and HDO mixing ratios using data from the ATMOS instrument. ATMOS, described in detail by *Farmer et al.* [1987], is a Fourier-transform infrared interferometer that gathered spectral absorption measurements at 0.01 cm^{-1} resolution from solar occultations on board four Space Shuttle missions (see *Gunson et al.* [this issue]). A previous report of HDO and CH_3D results from ATMOS was made by *Rinsland et al.* [1991] with data from the Spacelab 3 mission; however, their report did not relate changes in the CH_3D mixing ratio to those in HDO. With the combined Spacelab 3 and ATLAS-1, -2, and -3 missions, a much broader latitudinal coverage and many more vertical mixing ratio profiles were obtained, allowing characterization of the CH_3D and HDO budget on a more global basis. An important addition to previous reports is measurement of CH_3D inside the Arctic and Antarctic vortices. Above 28 km, the molecular density of CH_3D is normally too low to gain an adequate spectral absorption signal with the ATMOS instrument. However, the descent of upper stratospheric air to altitudes below 28 km inside the vortices [*Abrams et al.*, this issue a,b] allows measurement of CH_3D in "old" air that would be otherwise impossible to measure. As stratospheric dehydration is not the focus of this letter, we do not report measurements of HDO inside the polar vortices. Analyses are continuing on these vortex HDO measurements, and they will be the focus of an upcoming paper.

In this paper, the delta notation is used to describe isotopic fractionation as the difference in parts per thousand of an isotopically labelled species with respect to a standard, e. g.,

$$\delta D_{sample}\,(‰) = 1000 \times \frac{(D/H)_{sample} - (D/H)_{standard}}{(D/H)_{standard}}. \qquad (1)$$

Standard Mean Ocean Water (SMOW) is used for the standard D/H ratio (see IUPAC [1983]) and we use the recommended value of $(155.76\pm0.05)\times10^{-6}$ [*Hagemann et al.*, 1970].

Observations and data analysis

Information about ATMOS on the shuttle missions, and discussion of the mixing ratio retrieval process, can be found in *Gunson et al.* [this issue]. For the results described here, spectral lines of the ν_2 band of HDO and the ν_1 band of CH_3D were analyzed, and spectral intervals used for these analyses are described in Table 1. HDO is best observed in filters 2 (1100-

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Table 1. Spectral intervals and lines used for HDO and CH_3D analyses

Spectral interval center (cm^{-1})	Interval width (cm^{-1})	Altitude range (km)	Line center (cm^{-1})	Line intensity ($\times 10^{23}$ cm molec.$^{-1}$)	Air-broadened half-width (cm^{-1}/atm at 296K)	Ground-state energy (cm^{-1})	Temperature sensitivity of line intensity at 230K (% K^{-1})
CH_3D							
2950.84	0.24	10-28	2950.8514	2.81	0.072	266.3	0.07
3061.56	0.20	15-36	3061.4148	5.21	0.077	89.9	-0.4
3078.34	0.17	15-28	3078.3125	1.61	0.070	217.1	-0.07
			3078.3551	2.09	0.072	184.7	-0.2
3098.91	0.15	10-24	3098.8832	1.58	0.068	346.0	0.3
HDO							
1408.35	0.25	10-34	1408.3914	0.962	0.102	29.8	-0.6
1421.62	0.40	13-42	1421.6073	1 26	0.077	233.1	0.02
1439.93	0.32	15-40	1439.8887	1.54	0.095	150.1	-0.2
1451.40	0.34	10-29	1451.4597	1.21	0.093	265.2	0 07
1469.43	0.23	17-40	1469.3658	2.53	0.095	156 4	-0.2
1474.09	0 31	19-40	1474.1110	1 30	0.094	156.4	-0 2
1475.62	0.31	20-33	1475.5917	1 37	0.096	150.2	-0.2
1479.96	0 42	10-26	1480.0941	0 581	0.093	225.9	-0.04
1484.11	0.25	15-40	1484.1065	2.44	0.092	225.9	-0.04
1488.16	0.48	20-40	1488.0252	1 09	0.093	221.9	-0.04
			1488.1937	1 33	0.100	32.5	-0.6
1494.86	0.29	15-29	1494.8598	0.834	0.095	221.8	-0.05
1497.85	0.34	15-40	1497.8807	2.08	0.085	308.6	0.02

Note: The temperature dependence for air-broadened half-widths is $T^{-0.75}$ for CH_3D and $T^{-0.64}$ for HDO. Line parameters for CH_3D are from *Rinsland et al.* [1991]. HDO line parameters are discussed in *Brown et al* [1995].

2000 cm^{-1}) and 9 (600-2450 cm^{-1}), while CH_3D could only be observed in filter 3 (1580 - 3400 cm^{-1}). However, CH_4 can be analyzed in all of these filters and, with a correlation of CH_3D to CH_4 in filter 3, we are able infer the mixing ratio of CH_3D in filters 2 and 9 from CH_4 mixing ratios. At polar latitudes, determination as to whether a CH_3D measurement was inside or outside the vortex was based on visual inspection of co-located mixing ratio profiles of CH_4 and N_2O, as these gases show markedly smaller mixing ratios inside the vortex than outside at similar altitudes (see *Abrams et al.*, this issue a,b). "Vortex edge" observations were not used. CH_3D results are presented from tangent pressures of 100 mb to 17 mb, and HDO results are from 100 mb to 10 mb. Before final analyses, data were filtered by rejecting any observations with an estimated random error greater than 30% for CH_3D and HDO, or 10 % for CH_4. This step eliminated about 16% of the filter 3 CH_3D data and about 19% of the filter 2 and 9 HDO data. Systematic biases, mostly from errors in line intensities, are estimated to be 7% for CH_3D, 6% for HDO, and 5% for CH_4 (see *Abrams et al.*, this issue, c).

CH_3D measurement and the D/H ratio in methane

Rate constants for reactions of OH or Cl with CH_3D are lower than those for CH_4 [*DeMore et al.*, 1994; *Wallington and Hurley*, 1992], but any isotope effect between the rate constants of the excited $O(^1D)$ + CH_3D and that of $O(^1D)$ + CH_4 is expected to be relatively minor [*Kaye*, 1987]. To estimate these combined effects on the D/H ratio of methane, we begin by assuming that in the mid to lower stratosphere CH_4 and CH_3D are only destroyed by OH, Cl, and $O(^1D)$ oxidation, and photolysis is negligible. The oxidation of CH_3D and CH_4 can then be described by:

$$\frac{1}{[CH_3D]}\frac{d[CH_3D]}{dt} = -k^*_{OH}[OH] - k^*_{Cl}[Cl] - k^*_{O(^1D)}[O(^1D)], \quad (2)$$

$$\frac{1}{[CH_4]}\frac{d[CH_4]}{dt} = -k_{OH}[OH] - k_{Cl}[Cl] - k_{O(^1D)}[O(^1D)]. \quad (3)$$

Let $\gamma_i(T)$ equal the ratios of the rate constants. That is, $\gamma_{OH}(T)=k^*_{OH}/k_{OH}$, $\gamma_{Cl}(T)=k^*_{Cl}/k_{Cl}$ and $\gamma_{O(^1D)}(T)=k^*_{O(^1D)}/k_{O(^1D)}$, where T is temperature. Subtraction of Equation (3) from (2) gives:

$$\frac{1}{[CH_3D]}\frac{d[CH_3D]}{dt} - \frac{1}{[CH_4]}\frac{d[CH_4]}{dt} = -(\gamma_{OH}-1)k_{OH}[OH] - (\gamma_{Cl}-1)k_{Cl}[Cl] - (\gamma_{O(^1D)}-1)k_{O(^1D)}[O(^1D)]. \quad (4)$$

But we note that

$$k_{OH}[OH] = \frac{-1}{[CH_4]}\frac{d[CH_4]}{dt} f_{OH}(z), \quad (5)$$

where $f_{OH}(z)$ is the fraction of all CH_4 destroyed at altitude z that is destroyed by OH. With similar definitions for $f_{Cl}(z)$ and $f_{O(^1D)}(z)$, substitution in (4) for k_{OH}, k_{Cl}, and $k_{O(^1D)}$ (noting that they sum to unity) and rearrangement yield:

$$\frac{1}{[CH_3D]}\frac{d[CH_3D]}{dt} = \left(\gamma_{OH} f_{OH} + \gamma_{Cl} f_{Cl} + \gamma_{O(^1D)} f_{O(^1D)}\right)\frac{1}{[CH_4]}\frac{d[CH_4]}{dt}, \quad (6)$$

or:

$$\frac{1}{[CH_3D]}\frac{d[CH_3D]}{dt} = \kappa(T,z)\frac{1}{[CH_4]}\frac{d[CH_4]}{dt}, \quad (7)$$

where $\kappa(T,z)$ is the term inside the parentheses of (6). Note that the left hand side of Equation (7) is the time constant for destruction of CH_3D, or equivalently, its inverse lifetime. Thus, for a $\kappa(T,z) < 1$, the lifetime of CH_3D is longer than that of CH_4. We estimate an "average" κ in the mid to lower stratosphere by assuming average fractions for destruction (i.e., f_{OH}, f_{Cl}, and $f_{O(^1D)}$), and assuming that the ratios of the rate constants, γ, are constant with the temperature range in the mid to lower stratosphere and that mixing effects are minor. Integrating (6), assigning boundary conditions, and dividing by total molecular concentration to get mixing ratios (χ) yield:

$$\ln \chi(CH_3D) = \ln \chi_0(CH_3D) + \kappa_{av} \ln\left[\frac{\chi(CH_4)}{\chi_0(CH_4)}\right], \quad (8)$$

or equivalently,

$$\frac{\chi(CH_3D)}{\chi_0(CH_3D)} = \left(\frac{\chi(CH_4)}{\chi_0(CH_4)}\right)^{\kappa_{av}}, \quad (9)$$

where $\chi_0(CH_3D)$ and $\chi_0(CH_4)$ are the initial mixing ratios of these gases as they enter the stratosphere. A rough estimate of κ_{av} can be made if we set γ_{OH}=0.67 (averaged from 190K to 250K using the rate constants reported by *DeMore et al.* [1994]), γ_{Cl}= 0.735 (from the evaluation by *Wallington and Hurley* [1992] at 295K), and $\gamma_{O(^1D)}$=1 (see *Kaye* [1987]). Model calculations by one of us (RJS) indicate that between about 16 km and 30 km, about 50% of the destruction of CH_4 is by OH, 29% by Cl and 21% by $O(^1D)$. Substituting these laboratory data and model results, κ_{av}=0.78, suggesting that the lifetime of CH_3D is significantly longer than that of CH_4, and enrichment of deuterium in methane can occur as the CH_4 mixing ratio decreases. We emphasize that this is only a rough estimation as none of the experiments measuring the kine-

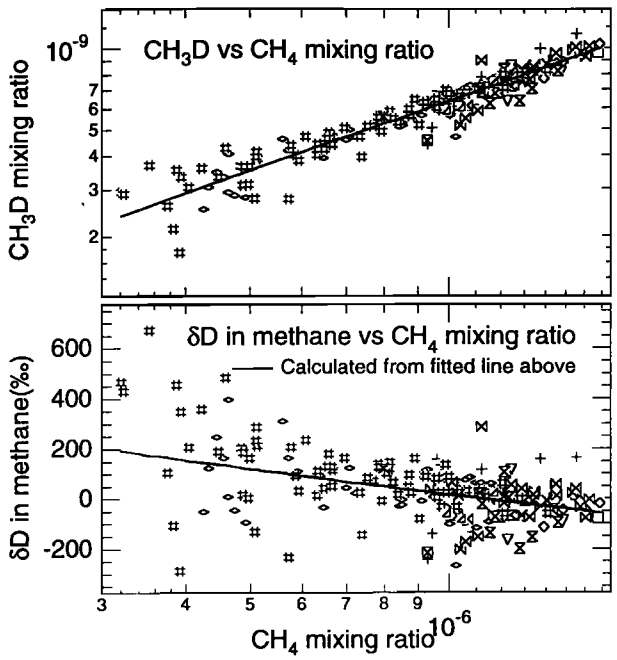

Figure 1. CH_3D mixing ratio vs CH_4 mixing ratio (upper panel) and δD in methane vs CH_4 mixing ratio (lower panel). For clarity, only one-sixth the data in extra-vortex regions are displayed. Spacelab 3: ⊠ 48°S, × 26°N-31°N; ATLAS-1: + 50°S-20°S; ATLAS-2: ▽ 50°S-25°S, ◿ 65°N- 70°N outside vortex, ◺ 65°N-70°N inside vortex; ATLAS-3: ⧖ 75°S-65°S outside vortex, # 75°S-65°S inside vortex, □ 0°-15°N, ◇ 15°N-30°N, ⋈ 30°N-50°N. Note: Some polar profiles had regions inside and some regions outside the vortex.

tic rate constants of OH or Cl with CH_3D were made at the cold temperatures typical of the lower stratosphere, and we are unaware of any laboratory measurements of the $O(^1D) + CH_3D$ rate constant.

ATMOS measurements of the mixing ratios of CH_3D are plotted against co-located measurements of CH_4 in the upper panel of Figure 1. We assume that $\chi_0(CH_4) = (1.71\pm0.03)\times10^{-6}$ (from global 1992 tropospheric measurements reported in *WMO* [1995], and where we have assumed a 2% error). From a best fit line of $\ln \chi(CH_3D)$ vs $\ln \chi(CH_4)$, we observe $\kappa_{av} = (0.84 \pm 0.02)$ (1σ combined precision and systematic error), which is higher than our initial estimate of 0.78. Note that the error in κ_{av} is not affected by systematic errors in the measured stratospheric mixing ratios of CH_3D and CH_4 (which instead affect the error in the intercept). On average, the stratospheric lifetime of CH_3D should be κ_{av}^{-1} (=1.19±0.02) times that of CH_4, or about 190 years based on a stratospheric CH_4 lifetime of 160 years [*Prather and Spivakovsky*, 1990]. From the fitted line at a tropospheric CH_4 mixing ratio of $(1.71\pm0.03)\times10^{-6}$, we find the mixing ratio of CH_3D entering the stratosphere to be $(9.9\pm0.8)\times10^{-10}$ (1σ combined precision and systematic error).

The lower panel of Figure 1 shows the enrichment of CH_3D with CH_4 mixing ratio, as well as the average enrichment calculated using the fitted line from the upper panel. Although there is considerable scatter in the data, it is seen that methane becomes progressively enriched in deuterium as the mixing ratio of CH_3D decreases. With a tropospheric CH_4 mixing ratio of $(1.71\pm0.03)\times10^{-6}$, the average δD in methane entering the stratosphere is –(71±74)‰ (1σ combined precision and systematic error). This is lower than, but within error of the ATMOS Spacelab 3 measurements of *Rinsland et al.* [1991] who found the average δD in methane from 18 to 28 km near latitudes of 30°N and 49°S to be –(49±44)‰ and +(24±125)‰ respectively. This is also within error of free tropospheric measurements by *Ehhalt* [1973], who reported values of –86‰ and –94‰, and *Wahlen et al.* [1987], who reported –(80±8)‰.

Measurement of HDO vs CH_3D and implications for HD

In the mid to lower stratosphere, atomic H is distributed primarily among CH_4, H_2O and H_2, with negligible amounts among other species. It appears that oxidation of H_2 is roughly balanced by its production via oxidation of CH_4 through a short-lived CH_2O intermediate [*Dessler et al*, 1994; *Abbas et al.*, this issue]. Similarly, deuterium is most likely distributed mainly among CH_3D, HDO, and HD (with HD produced by oxidation of CH_3D and destroyed by oxidation to HDO). However, in the mid to lower stratosphere, it may not necessarily be the case that the mixing ratio of HD is as weakly varying as that of H_2. As suggested by *Ehhalt et al.* [1989], the lower reaction rate constant of OH and HD compared to that of OH and H_2 may serve to enrich tropospheric hydrogen gas in deuterium. However, stratospheric destruction of HD is regulated not only by rates of OH attack, but also to a large extent by those of $O(^1D)$, and the rate constant of the $O(^1D)$ reaction is not expected to be significantly affected by deuterium substitution [*Kaye*, 1987]. (Reaction with Cl is a much more minor sink for hydrogen than for methane using the rate constants given by *DeMore et al.* [1994].) For production of HD, account must be taken of not only the oxidation rates of CH_3D, but also the partitioning of D in the short-lived species in the reaction pathway from CH_3D to HD (e.g. the yield of CH_2D vs CH_3, or that of CHDO vs CH_2O). In the absence of direct measure-

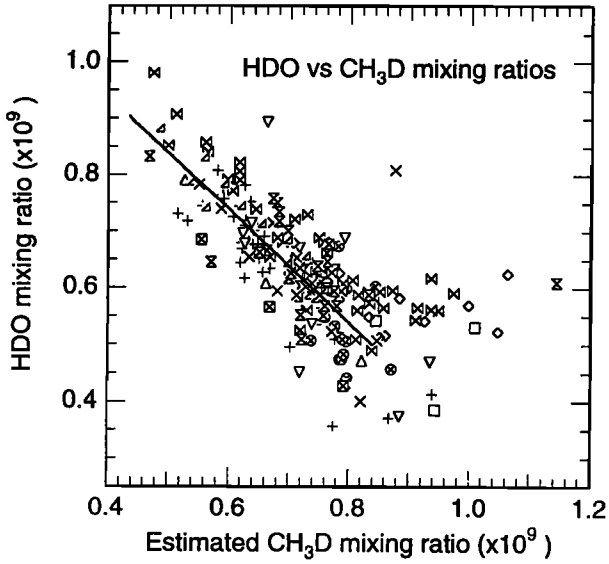

Figure 2. HDO mixing ratio vs CH_3D mixing ratio. The line is fitted only where the CH_4 mixing ratio is less than 1.4×10^{-6}. For clarity, only one-third the data for each latitude bin are shown. Spacelab 3: ⊠ 49°S, × 26°N-31°N; ATLAS-1: + 55°S-30°S, ⊗ 10°S-15°N, △ 15°N-30°N; ATLAS-2: ▽ 50°S-30°S, ◿ 65°N-70°N, outside vortex; ATLAS-3: ⧖ 75°S-65°S, outside vortex, □ 12°N, ◇ 15°N-30°N, ⋈ 30°N-50°N.

ment of HD, a test for changes in the HD mixing ratio is examination of those for HDO and CH_3D. Assuming the sum of the mixing ratios of HDO, CH_3D, and HD is constant, then:

$$\frac{d\chi(HDO)}{d\chi(CH_3D)} + \frac{d\chi(HD)}{d\chi(CH_3D)} = -1, \quad (10)$$

and any deviation of $d\chi(HDO)/d\chi(CH_3D)$ from -1 through the mid and lower stratosphere implies a changing mixing ratio of HD.

In order to compare HDO and CH_3D mixing ratios, which are not measured simultaneously, we use the relationship in Equation 8, with $\kappa=0.84\pm0.02$, $\chi_0(CH_4) = (1.71\pm0.03)\times10^{-6}$, and $\chi_0(CH_3D)=(9.9\pm0.8)\times10^{-10}$, to estimate the CH_3D mixing ratio from measurements of CH_4. Figure 2 is a scatter plot of the HDO mixing ratio in filters 2 and 9 versus this derived CH_3D mixing ratio. We calculate $d\chi(HDO)/d\chi(CH_3D)$ by a least-squares straight line fit to data where CH_4 mixing ratios were less than 1.4×10^{-6} to avoid seasonal effects in HDO in the lower stratosphere. The calculated slope, $-(1.0\pm0.1)$ (1σ combined precision and systematic error), indicates that HDO production is in near balance with CH_3D destruction. The error in the slope constrains the production of HD to be ±0.1 molecules HD created for each CH_3D molecule destroyed; however, as only about 10% of stratospheric deuterium is in HD, significant changes in the HD mixing ratio are still possible within this error. Large effects may also occur in the D/H ratio of stratospheric molecular hydrogen, but this would also be dependent on even minor changes in the H_2 mixing ratio due to H_2 photolysis or CH_4 oxidation (see, for example, *Dessler et al.* [1994]). The results in this report provide constraints for changes in HD below about 10 mb. To illustrate this, we assume a constant H_2 mixing ratio of 0.5×10^{-6} and a δD in hydrogen entering the stratosphere of +(70±30)‰ [*Friedman and Scholz*, 1974], which gives an initial HD mixing ratio of $(1.67\pm0.05)\times10^{-10}$. Assuming that CH_3D enters the stratosphere at a mixing ratio of 9.9×10^{-10}, then results here indicate that for each 1% decrease in the CH_3D mixing ratio, the percentage change in the HD mixing ratio from its tropospheric value is constrained to be ±0.6% and the change in δD in molecular hydrogen can be constrained to ±6‰ (1σ).

Conclusions

We have analyzed ATMOS spectra for mid to lower stratospheric HDO and CH_3D mixing ratios. The average D/H ratio in methane entering the stratosphere was found to be $-(71\pm74)$‰, but as the lifetime for CH_3D is greater than that of CH_4 by a factor of (1.19±0.02), this D/H ratio increases as methane becomes oxidized. Stratospheric production of HDO is (1.0±0.1) times that of CH_3D loss, and assuming deuterated species other than HDO, CH_3D and HD are in negligible abundance, changes in HD abundance are thus constrained to be ±0.1 molecules HD per molecule CH_3D destroyed (1σ combined precision and systematic error). To better understand these phenomena, research is warranted into the partitioning of deuterium in CH_3D destruction products (including a comparison of the photolysis rates of CHDO vs that of CH_2O), and direct stratospheric measurements of the HD mixing ratio.

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